EG&G IDAHO, INC.
ENVIRONMENTAL RESTORATION PROGRAM
SAMPLE MANAGEMENT OFFICE

STANDARD OPERATING PROCEDURE NO. SMO-SOP-12.1.4

VALIDATION OF GAS CHROMATOGRAPHIC DATA

For use in the validation of
organochlorine pesticide/PCB,
organophosphorus pesticide,
and organochlorine herbicide
data using USEPA Contract Laboratory Program
protocols

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Prepared by:

R. D. Grant, Scientist, ERP SMO — Date

Reviewed by:

J. P. Shea, Chairman, ERP Independent Review Committee — Date

Approved by:

D. J. Yurman, Acting Manager,
Data Management Unit — Date

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1. PURPOSE AND SCOPE

This document is a standard operating procedure (SOP) designed to offer guidance in the evaluation and validation of gas chromatographic data.

The specific areas covered by this SOP include holding times, instrument performance, calibrations, blanks, surrogates, field duplicates, matrix spikes, compound identification, compound quantitation, reported detection limits, and final assessment for the sample delivery group (SDG).

2. ACRONYMS/DEFINITIONS

COC	Chain of Custody
ERP	Environmental Restoration Program
GC	Gas Chromatography
L&V	Limitations and Validation
MS	Matrix Spike
MSD	Matrix Spike Duplicate
QC	Quality Control
RPD	Relative Percent Differences
RQL	Required Quantitation Limit
RSD	Relative Standard Deviation
SDG	Sample Delivery Group
SMO	Sample Management Office
SOP	Standard Operating Procedure
CF	Calibration Factor
Primary analysis	One of two types of compound analysis by GC/EC techniques, the other being confirmation analysis. If the two analyses are run at separate times, the primary analysis is the first analysis chronologically and is used to establish the tentative identification of any target compounds detected. The identification is then confirmed in the confirmation analysis. If the two analyses are performed simultaneously, either may be considered the primary analysis. Either may be used for quantitation if contract criteria are met.
QA	Quality assurance - Total program for ensuring the reliability of data.
QC	Quality control - Route application of procedures for controlling the monitoring process.

RPD Relative percent difference (between matrix spike and matrix spike duplicate)

RT Retention Time

SDG Sample delivery group - Defined by one of the following, whichever occurs first:

- Project of field samples
- Each group of 20 field samples with a project
- Each 14-day calendar period during which field samples in a project are received, beginning with receipt of the first sample in the SDG.

3. DESCRIPTION

SDGs routinely have unique samples that require special attention by the reviewer. Field blanks, field duplicates, equipment rinsates, and performance audit samples need to be identified. The sampling records (field log books, chain-of-custody (COC) records etc.) should provide:

- A project officer for the site
- A complete list of samples with notations on:
  - Sample matrix
  - Blanks
  - Field duplicates, if applicable
  - Field spikes, if applicable
  - Quality control (QC) audit sample, if applicable
  - Shipping dates
  - Laboratory name
  - Preservation information.

The COC record includes sample descriptions and the date of sampling. The reviewer must take into account lag times between sampling and shipping while assessing sample holding times.

The narrative is another source of general information. Notable problems with matrices, insufficient sample volume for analysis or reanalysis, and unusual events should be found in the narrative.

4. PRECAUTIONS/LIMITATIONS

The reviewer should have experience in gas chromatography (GC) analyses and data review and a general overview of the SDG in order to use this SOP effectively. The exact number of samples, their assigned numbers and sample matrix are essential information. Background information on the site is helpful but is often difficult to locate. The EG&G Idaho Environmental Restoration Program (ERP) Sample Management Office (SMO) is the best source for this information (for ERP projects), answers, or further direction.

The most restrictive validation flag must always be assigned to the data in all instances where the data requires qualification for more than one reason. For example, non-detect data that must be flagged as rejected "R" because of holding time violations and must also be qualified with the quantitation flagged as estimated "UJ" must always be flagged as rejected "R".

5. GAS CHROMATOGRAPHIC PROCEDURE

The following are the requirements (listed by section) to be checked for validation:

I. Holding Times

II. Instrument Performance

III. Calibration

- Initial
- Analytical Sequence
- Continuing

IV. Blanks

V. Surrogate Recovery

VI. Matrix Spike/Matrix Spike Duplicate (MS/MSD)

VII. Field Duplicates

VIII. Compound Identification

IX. Quantitation and Reported Detection Limits

X. Overall Assessment of Data for an SDG

I. HOLDING TIMES

A. Criteria

The EG&G Idaho ERP SMO requirements for sample holding times are as follows:

Soils/Sediments/sludges: All samples must be extracted within 14 days of sample collection. Extracts must be analyzed within 40 days of sample extraction. Samples and extracts must always be stored at 4°C.

Water: All samples must be extracted within 7 days of sample collection. Extracts must be analyzed within 40 days of sample extraction. Samples and extracts must always be stored at 4°C.

B. Evaluation Procedure

Actual holding times are established by comparing the sample collection date on the EG&G Idaho COC form with the dates of extraction and analysis on Form I. Examine the sample records (COC form, field logbooks etc.) to determine if the samples were properly preserved. It must be assumed that the samples are unpreserved if there is no indication of preservation in the sampling documentation.

C. Action

If holding times are exceeded, flag all positive results as estimated (J) and sample quantitation limits as estimated (UJ) and state in the final report that holding times were exceeded.

If holding times are exceeded by more than double the allowable holding time, flag non-detect data as unusable (R) and flag all positive results as estimated (J)

II. INSTRUMENT PERFORMANCE

A. Criteria

1. Retention Time Windows

   The laboratory must report retention time window data on the standards summary (Form IX) for each GC column used to analyze samples.

2. Surrogate Retention Time Check

   The retention time of the surrogate compound in each analysis must be compared to the retention time of the surrogate in Evaluation Standard Mix A. The percent difference between the retention time of the surrogate compound in a given analysis and the retention time of the surrogate compound in Evaluation Standard Mix A must

not exceed 2.0% for packed columns, 0.3% for narrow-bore capillary columns, and 1.5% for wide-bore capillary columns. The percent difference (%D) is calculated using the following equation:

$$\%D = \frac{RT_I - RT_S}{RT_I} \times 100 \qquad (1)$$

where

RT_I = absolute retention time of surrogate in the initial standard (Evaluation Standard Mix A)

RT_s = absolute retention time of surrogate in the subsequent analyses.

B. Evaluation Procedure

1. Check raw data to verify that the retention time windows are reported on Form IX, and that all standards are within the established retention time windows.

2. Check raw data to verify that the percent difference in retention time for the surrogate in all standards and samples is $\leq$2.0% for packed column analysis, $\leq$0.3% for capillary column analysis, and $\leq$1.5% for wide-bore capillary column analysis on Form VIII.

C. Action

1. Retention Time Windows

Retention time windows are used for qualitative identification of target compounds. Sample results should be carefully evaluated if the associated standards do not fall within the retention time windows. All samples injected after the last in-control standard are potentially affected.

a. Check to see if the chromatograms of the affected samples contain any peaks within an expanded window surrounding the expected retention time window of the compound of interest. There is usually no effect on the data if no peaks are present either within or close to the retention time window of the deviant target compound therefore non-detected values can be considered valid.

b. The reviewer has two options for determining the extent of the effect on the data if the affected sample chromatograms contain peaks that may be of concern [i.e., above the Required Quantitation Limit (RQL) and either close to or within the expected retention time window of the target analyte of interest].

1) In some cases, additional effort is warranted by the reviewer (e.g., if the data are needed on a priority basis and if the peak(s) present might represent a level of concern for that particular compound). In these situations, the reviewer may undertake the following additional efforts to determine a usable retention time window for affected samples:

   (a) The reviewer should examine the data package for the presence of three or more standards containing the compound of interest that were run within the period during which the sample was analyzed.

   (b) If three or more such standards are present, the mean and standard deviation of the retention time window can be reevaluated.

   (c) The valid positive or negative sample results can be determined using the reevaluated window if all standards and matrix spikes fall within the revised retention time window. Flag all positive results and quantitation limits as unusable (R) if all standards and matrix spikes do not fall within the revised retention time window. The final report should emphasize the possibility of either false negatives or false positives, as appropriate.

   (d) The narrative should identify the additional efforts taken by the reviewer and the resultant impact on data usability. In addition, the support documentation should contain all calculations and comparisons generated by the reviewer.

2) Flag all positive results and quantitation limits as unusable (R) if no additional effort is warranted by the reviewer. The final report should emphasize the possibility of either false negatives or false positives, as appropriate.

2. Retention Time Check

   a. If the retention time shift for the surrogate is >2.0% for packed column, >0.3% for narrow-bore capillary column, or >1.5% for wide-bore capillary column, the analysis shall be flagged unusable for that sample(s) (R).

b. The retention time shift cannot be evaluated in the absence of the surrogate or if the surrogate cannot be seen because of dilution. State in the L&V report that no evaluation of instrument performance based on surrogate recovery can be made in the absence of the surrogate compound and that the impact on data usability is unknown.

III. CALIBRATION

A. Criteria

1. Initial Calibration Linearity Check

The percent relative standard deviation (%RSD) of calibration factors for all target compounds and surrogates must not exceed 10%. The calibration factor is calculated using the following equation:

$$\text{Calibration Factor} = \frac{\text{Total Area of Peak}}{\text{Mass Injected (ng)}}. \quad (2)$$

The %RSD is calculated using Equations (3) and (4).

$$\sigma = \sqrt{\sum_{i=1}^{n} \frac{(x_i - \bar{x})^2}{(n-1)}} \quad (3)$$

$$\%RSD = \frac{\sigma}{CF} \cdot 100 \quad (4)$$

where

σ = standard deviation

CF = calibration factor

NOTE: The 10% RSD linearity check is required only for columns that are used for quantitative determinations. Quantitation of the surrogate requires the use of a column shown to meet the 10% linearity criterion. Columns used only to provide qualitative confirmation are not required to meet the 10% linearity criterion.

2. Analytical Sequence

a. Primary Analysis

All standards must be analyzed at the beginning of each analytical sequence.

b. Confirmation Analysis

1) Evaluation Standard Mix A, B, and C are required for the curve.

2) Only the standards containing the compound(s) to be confirmed are required. These standards must be repeated after every five samples.

3) Evaluation Standard Mix B is required after every ten samples.

3. Continuing Calibration

The calibration factor for each standard must be within 15% of the standard at the beginning of the analytical sequence on quantitation columns (20% on confirmation columns).

B. Evaluation Procedure

1. Initial Calibration

a. Inspect the appropriate evaluation standards summary (Form VIII) and verify agreement with the raw GC data (chromatograms and data system printouts).

b. Check the raw data and recalculate some of the calibration factors and the %RSD for the target compounds and surrogates at the three calibration concentrations.

c. Verify that the %RSD for the calibration factor of each specific compound is less than or equal to 10% for each analytical sequence.

d. Perform a more comprehensive recalculation if calculation errors are detected.

2. Verify that all standards were analyzed as specified in the method.

3. Continuing Calibration

a. Review the compound sample data to verify whether the standard was used as a quantitation standard or as a confirmation standard.

b. For the quantitation standards, check the raw data to verify the percent difference (%D), using the following formula, for approximately 10% of the reported values by recalculation.

$$\%D = \frac{R_1 - R_2}{R_1} \quad (5)$$

where

R_1 = calibration factor from first analysis

R_2 = calibration factor from second analysis.

C. Action

1. Initial Calibration

   Flag all associated quantitative results as estimated (J) if criteria for linearity are not met.

2. Analytical Sequence

   Data may be affected if the proper standards have not been analyzed. The data reviewer must use professional judgment to determine severity of the effect and to qualify the data accordingly.

3. Continuing Calibration

   a. Flag all associated positive quantitative results as estimated (J) if the percent difference between calibration factors is >15% for the compound(s) being quantitated (20% for compounds being confirmed).

IV. BLANKS

A. Criteria

No contaminants should be present in the blank(s).

B. Evaluation Procedure

1. Review the results of all associated blank(s), Form(s) I, and raw data (chromatograms, quantitation reports, or data system printouts).

2. Verify that the method blank analysis(es) contain(s) less than the RQL of any compound or interfering peak.

3. Verify that method blank analyses have been reported per matrix, per concentration level, for each GC system used to analyze samples and for each extraction batch.

C. Action

Action in the case of unsuitable blank results depends on the circumstances and the origin of the blank. No positive sample results should be reported unless the concentration of the analyte in the sample exceeds five times the amount in the blank. In instances where more than one blank is associated with a given sample, qualification should be based on a comparison with the associated blank having the highest concentration of a contaminant. The results must not be corrected by subtracting the blank value. Specific actions are as follows:

1. If a target compound is found in the blank but not found in the sample(s), no action is taken.

2. Any target compound detected in the sample and also detected in any associated blank must be qualified when the sample concentration is less than five times the blank concentration.

   The reviewer should note that the blank analyses may not involve the same weights, volumes, or dilution factors as the associated samples. These factors must be taken into consideration when applying the five times criteria, such that a comparison of the total amount of contamination is actually made.

   Additionally, there may be instances where little or no contamination was present in the associated blanks, but qualification of the sample was deemed necessary. Contamination introduced through dilution solvent is one example. Although it is not always possible to determine, instances of this occurring can be detected when contaminants are found in the diluted sample result but are absent in the undiluted sample result. Since both results are not routinely reported, it may be impossible to verify this source of contamination. The reviewer should qualify the data when it is determined that the contamination is from a source other than the sample. In this case, the five times rule does not apply; the sample value should be reported as a non-detect.

3. The following are examples of applying the blank qualification guidelines.

Case 1: Sample result is greater than the RQL but less than the required amount (5x) from the blank result.

	5x
Blank result	1.0
RQL	0.5
Sample result	4.0
Qualified sample result	4.0U

In this case, sample results less than 5.0 (or 5 x 1.0) would be qualified as non-detects.

Case 2: Sample result is greater than the required amount (5x) from the blank result.

	5x
Blank result	1.0
RQL	0.5
Sample result	6.0
Qualified sample result	6.0

V. SURROGATE RECOVERY

A. Criteria

Sample and blank recoveries of surrogate compounds must be within the limits indicated in the analytical method (Form II).

B. Evaluation Procedure

1. Check the raw data (e.g., chromatograms, quantitation list) to verify the recoveries on the surrogate recovery form (Form II).

2. Check the raw data for possible interferences that may have affected surrogate recoveries if surrogate recoveries are not within the required recovery limits.

C. Action

The following guidance is suggested if surrogate recoveries are outside of advisory windows:

1. Flag associated positive results and quantitation limits as estimated (J) if low recoveries are obtained.

2. Use professional judgment to determine appropriate action if high recoveries are obtained. A high bias may be due to coeluting interferences.

3. If zero surrogate recovery is reported, the reviewer should examine the sample chromatogram to determine if the surrogate may be present but slightly outside its retention time window. If this is the case, in addition to assessing surrogate recovery for quantitative bias, the overriding consideration is to investigate the qualitative validity of the analysis. If the surrogate is not present, flag all negative results as unusable (R).

VI. MATRIX SPIKE/MATRIX SPIKE DUPLICATE

A. Criteria

1. Advisory limits are established for spike recovery limits in the analytical method and on Form III.

2. Advisory limits are established for the RPD between MS/MSD recoveries in the analytical method and on Form III.

B. Evaluation Procedure

1. Inspect results for the MS/MSD recovery (Form III).

2. Verify transcriptions from the raw data and verify calculations.

C. Action

No action is taken on MS/MSD data alone to qualify an entire SDG. However the data reviewer may use MS/MSD results in conjunction with other QC criteria and determine the need for some qualification of the data.

The data reviewer should first try to determine to what extent the results of the MS/MSD affect the associated data. This determination should be made with regard to the MS/MSD sample itself as well as specific analytes for all samples associated with the MS/MSD. All qualification of data based on MS/MSD results should be documented in detail in the Limitations and Validation (L&V) report.

VII. FIELD DUPLICATES

A. Criteria

There are no specific review criteria for field duplicate analyses comparability.

B. Evaluation Procedures

Field duplicates should be identified using EG&G Idaho COC forms or sample field logbooks. The reviewer should compare the positive results reported for each sample and calculate the Relative Percent Differences

(RPD). The final L&V report should mention incidences of one sample of a duplicate pair having a positive result and the other sample of the duplicate pair having non-detect results (whether due to different dilution or not).

C. Action

Report the RPD between field duplicates in the L&V report. Evaluation of the field duplicate data will be made by the appropriate EG&G Idaho ERP project management personnel.

VIII. COMPOUND IDENTIFICATION

A. Criteria

Retention times of reported compounds must fall within the calculated retention time windows for the two chromatographic columns.

B. Evaluation Procedure

1. Review Form I, the associated raw data (chromatograms and data system printouts), and the appropriate compound identification summary (Form X). Confirm reported positive results, using appropriate retention times and retention time windows, and verify that the compounds listed as "not detected" are correct.

2. Verify that positive identifications have dissimilar column analysis.

C. Action

All reported positive results should be considered non-detects if the qualitative criteria for two-column confirmation were not met. The reviewer should use professional judgment to assign an appropriate quantitation limit using the following guidance:

1. The RQL can be reported and flagged as non-detect "U" if the misidentified peak was sufficiently outside the target compound retention time window.

2. The reported value should be considered and flagged as having an estimated quantitation limit (UJ) if the misidentified peak poses an interference with potential detection of a target peak, .

IX. QUANTITATION AND REPORTED DETECTION LIMITS

A. Criteria

Quantitation, as well as the adjustment of the RQL, must be calculated according to the analytical method.

B. Evaluation Procedure

1. Raw data should be examined to verify the correct calculation of all sample results reported by the laboratory. Quantitation reports, chromatograms, and sample preparation logsheets should be compared to the reported positive sample results and quantitation limits.

2. Verify that the RQLs have been adjusted to reflect all sample dilutions, concentrations, splits, cleanup activities, and dry-weight factors that are not accounted for by the method.

C. Action

Quantitation limits affected by large, off-scale peaks should be flagged as unusable (R). The reviewer can provide an estimated quantitation limit (UJ) for each affected compound if the interference is on-scale.

NOTE: Results can be checked for rough agreement between quantitative results obtained on the two GC columns. The reviewer should use professional judgment to decide whether a much larger concentration obtained on one column versus the other indicates the presence of an interfering compound. The lower of the two values should be reported and qualified as presumptively present at an estimated quantity (NJ) if an interfering compound is indicated. This necessitates a determination of an estimated concentration on the confirmation column. The L&V report should indicate that the presence of interferences has obscured the attempt at a second-column confirmation.

X. OVERALL ASSESSMENT OF DATA FOR AN SDG

It is appropriate for the data reviewer to make professional judgments to and express concerns and comments on the validity and the overall usability of the data contained in an SDG. This is particularly appropriate for SDGs in which there are several QC criteria out of specification. The additive nature of QC factors out of specification is difficult to assess in an objective manner, but the reviewer has a responsibility to inform users concerning data quality and data limitations to assist the user in avoiding inappropriate use of the data, while not precluding any consideration of the data at all.

GLOSSARY A

DATA QUALIFIER DEFINITIONS

For the purposes of this document, the following code letters and associated definitions are provided.

U - The material was analyzed for but was not detected. The associated numerical value is the sample quantitation limit.

J - The analyte was positively identified in the sample, but the associated numerical value may not be an accurate representation of the amount actually present in the environmental sample. The data should be seriously considered for decision-making and are usable for many purposes.

A subscript may be added to the "J" flag to indicate which of the following quality control criteria were not met:

J_1) Blank contamination: indicates high bias and/or false positives

J_2) Calibration range exceeded: indicates possible low bias.

J_3) Holding times not met: indicates results are biased low.

J_4) Other QC outside control limits: indicates that bias is not readily determined.

R - The data are unusable (may or may not be present). Resampling and reanalysis are necessary for verification.

N - Presumptive evidence of the presence of the material.

NJ - Presumptive evidence of the presence of the material at an estimated quantity.

UJ - The material was analyzed for but was not detected. The sample quantitation limit is an estimated quantity.

The reviewer must explain and thoroughly document the use of any qualifiers other than the ones listed above.

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STANDARD OPERATING PROCEDURE

FOR

INORGANIC DATA VALIDATION

NO. SMO-SOP-12.1.5

EG&G Idaho, Inc.
Environmental Restoration Program

Sample Management Office

Prepared by:

R. J. Sheehan, Scientist, ERP SMO — August 9, 1991 Date

Reviewed by:

J. P. Shea, Chairman
ERP Independent Review Committee — 10/1/91 Date

Approved by:

J. E. Ferguson, Manager
Data Management Unit — 10/2/91 Date

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SMO-SOP-12.1.5

STANDARD OPERATING PROCEDURE

FOR

INORGANIC DATA VALIDATION

September 1991

Environmental Restoration Program
Idaho National Engineering Laboratory
EG&G Idaho, Inc.
Idaho Falls, Idaho 83415

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CONTENTS

STANDARD OPERATING PROCEDURE FOR INORGANIC DATA VALIDATION

1. PURPOSE AND SCOPE

This document[1] is designed to offer guidance in laboratory data validation. Data validation is the process of evaluating the quality and reliability of data from laboratory analysis. Due to the complexities and uniqueness of data relative to specific samples and/or different types of analyses, some areas of this standard operating procedure (SOP) are only able to offer general guidance rather than step-by-step procedures. Various generally accepted good laboratory practices (GLP) for inorganic tests will provide the data validator with much of the criteria needed to validate data from nonroutine inorganic analyses.

Those areas where specific step-by-step procedures are possible are primarily areas in which definitive performance requirements are established. These requirements are concerned with specifications that are not sample dependent; they specify performance requirements on matters that should be fully under a laboratory's control. These specific areas include blanks, calibration standards, calibration verification standards, laboratory control standards, and interference check standards.

This document is intended mainly for technical review; however, contract compliance must also be addressed because many areas of the technical review naturally overlap with contract compliance criteria. The inorganic Contract Laboratory Program (CLP) statement of work (SOW) is the quintessence of the establishment of definitive performance requirements. The CLP SOW is the only inorganic document that has a set of validation guidelines[2] that are accepted and used on a nationwide scale for validating laboratory data. CLP data validation is based on identifying degrees of variance from established norms.[3] Although these norms might, at times, seem arbitrary, their intention is to set some analytical quality control (QC) limit that, if exceeded, may

compromise the quality of the data. Many of the CLP performance requirements are routinely used as criteria for validating non-CLP analytical data.

A contract laboratory submitting data that are out of specification may be required to rerun or resubmit data, even if the previously submitted data have been used because of urgent program needs; data that do not meet specified requirements are never fully acceptable. The only exception to this requirement is in the area of requirements for individual sample analysis; if the nature of the sample itself limits the attainment of specifications, appropriate allowances must be made.

2. ACRONYMS/DEFINITIONS

AA	atomic absorption spectrometry
accuracy	Accuracy measures the bias in a measurement system; it is difficult to measure for the entire data collection activity. Sources of error are the sampling process, field contamination, preservation, handling, sample matrix, sample preparation, and analysis techniques. Sampling accuracy may be assessed by evaluating the results of field/trip blanks; analytical accuracy may be assessed through use of known and unknown QC samples and matrix spikes.
analyte	The element, ion, compound, or aggregate property of a sample an analysis seeks to determine.
analytical curve	Synonymous with calibration curve.
analytical spike	The furnace post-digestion spike. The addition of a known amount of analyte after digestion.
associated samples	Any sample related to a particular QC analysis. For example: - For ICV, all samples run under the same calibration curve. - For duplicate RPD, all SDG samples digested/distilled of the same matrix.

calibration curve	A plot of instrument response versus concentration of standards.
case	A finite, usually predetermined number of samples collected in a given time period for a particular site. A case consists of one or more sample delivery groups.
CCB	continuing calibration blank - A deionized water sample (preserved like the calibration standards) run every 10 samples; designed to detect any carryover contamination.
CCS	contract compliance screening - A process in which SMO inspects analytical data for contractual compliance.
CCV	continuing calibration verification - A standard run every 10 samples; designed to test instrument performance.
CLP	Contract Laboratory Program
COC	chain of custody
completeness	The percentage of measurements made that are judged to be valid measurements.
CRDL	contract required detection limit
CTR	contract and technical review
CV	coefficient of variation

data package	A collection of information that includes data for analysis of all samples in one SDG, including field and analytical samples, reanalyses, blanks, spikes, duplicates, and laboratory control samples.
data validation	The process of evaluating the quality and reliability of data from laboratory analysis.
DQO	data quality objective
EMSL/LV	Environmental Monitoring System Laboratory/Las Vegas (P.O. Box 15027, Las Vegas, Nevada 89114)
EPA	Environmental Protection Agency
ERP	Environmental Restoration Program (EG&G Idaho, Inc.)
field blank	Field blanks are intended to identify contaminants that may have been introduced in the field. Examples are trip blanks, travel blanks, rinsate blanks, and decontamination blanks.
field duplicate	A duplicate sample generated in the field, not in the laboratory.
finding	A deficiency in the data that requires one or more parameters to be given a validation qualifying flag.
GLP	good laboratory practice

holding time	The time from sample collection to laboratory analysis. For some analyses, the time from sample collection to sample preparation must also be considered.
ICB	initial calibration blank - First blank standard run to confirm the calibration curve.
ICP	inductively coupled plasma atomic emission spectrometry
ICS	interference check sample
ICV	initial calibration verification - First standard run to confirm the calibration curve. (NOTE: The ICV is made from a source that is independent from the source used to make the calibration standards.)
IDL	instrument detection limit
initial calibration	The establishment of a calibration curve with the appropriate number of standards and concentration range. The calibration curve plots instrument response versus concentration of standards.
IRDA	inorganic regional data assessment
laboratory qualifying flag	A letter or symbol that represents a particular meaning, and is assigned to an individual data point by the laboratory in order to alert data users to either the method employed, concentration range achieved, or a potential or real problem associated with the reported value.

For example:

P - The sample was analyzed by ICP.

B - The reported value was obtained from a reading < CRDL but ≥ IDL.

U - The analyte was analyzed for but not detected.

E - The reported value is estimated because of the presence of interference.

M - Duplicate injection precision was not met.

N - Spiked sample recovery was not within control limits.

S - The reported value was determined by MSA.

W - The analytical spike is outside the control limits (85 to 115%), while sample absorbance is less than 50% of spike absorbance.

* - Duplicate analysis is not within control limits.

+ - Correlation coefficient for the MSA is less than 0.995.

LCS laboratory control sample

L&V	data limitations and validation (L&V) report - Report written by an analytical chemist or other technical expert performing method validation. The report documents any deficiencies in the data identified during the data validation process. The report also indicates the analytical level at which the data were obtained and the level of validation performed on the data.
matrix	The predominant material of which the sample to be analyzed is composed. Matrix is not synonymous with phase (liquid or solid).
MS	matrix spike - Introduction of a known concentration of an analyte into a sample to provide information about the effect of the sample matrix on the digestion and measurement methodology.
MSA	method of standard addition
observation	A deficiency in the data that requires no validation qualifying flags but, if corrected, would improve the product.
post digestion spike	The addition of a known amount of analyte after digestion. (Also identified as analytical spike, or spike for furnace analyses.)
precision	Precision measures the reproducibility of measurements under a given set of conditions. Specifically, it is a quantitative measure of the variability of a group of measurements compared to their average value. Precision is

	usually stated in terms of standard deviation but other estimates, such as the coefficient of variation (relative standard deviation), range (maximum value minus minimum value), and relative range, are common.
professional judgement	Intuition that is a cumulative result of scientific and technical training, experience in analytical testing and reporting, and a good understanding of specific method-required QA/QC procedures.
QA/QC	quality assurance/quality control
RAS	routine analytical services
raw data	Data that are needed to complete all data package reporting forms and contract requirements. (instrument printouts, standard sources and preparation dates, sample preparation and digestion, distillation logs, chain-of-custody forms, etc.)
RPD	relative percent difference
RSD	relative standard deviation
SAP	sampling and analysis plan
SAS	special analytical services
SDG	sample delivery group - Defined by one of the following, whichever occurs first: - Case of field samples

- Each 20 field samples in a case

- Each 14-day calendar period during which field samples in a case are received, beginning with receipt of the first sample in the SDG.

serial dilution	A sample run at a specific dilution to determine whether any significant chemical or physical interferences exist due to sample matrix effects.
SMO	Sample Management Office
SOP	standard operating procedure
SOW	statement of work
TAL	target analyte list
validation qualifier flag	A letter or letters, that represent a particular meaning and that are assigned to an individual data point by the data validator in order to alert data users to a potential or real problem associated with the reported value. For example:

U - The material was analyzed for, but was not detected above the level of the associated value. The associated value is either the sample quantitation limit or the sample detection limit.

J - The analyte was analyzed for and was positively identified, but the associated

numerical value may not be consistent with the amount actually present in the environmental sample.

R - The data are unusable. (NOTE: Analyte may or may not be present.)

UJ - The material was analyzed for, but was not detected. The associated value is an estimate and may not accurately reflect the IDL in the sample matrix. (NOTE: See Reference 4 for definitions of data qualifier flags.)

3. DESCRIPTION

In order to use this document effectively, the reviewer should have a general overview of the case at hand. The exact number of samples, their assigned numbers, their matrix, and the number of laboratories involved in their analysis are essential information. Background information on the site is helpful, but often this information is very difficult to locate. The site project officer is the best source for answers or further direction.

Contract compliance screening (CCS) is a source of a large quantity of summarized information. It can be used to alert the reviewer of problems in the case or what may be sample-specific problems. This information may be used for data validation. If CCS is unavailable, those criteria affecting data validity must be addressed by the data reviewer.

Cases routinely have unique samples that require special attention when reviewed. Field blanks, field duplicates, and performance audit samples need to be identified for the validator if they are to be considered in the validation report. The sampling records should provide:

- Project officer for site
- Complete list of samples with notations on:
  - Sample matrix
  - Blanks[a]
  - Field duplicates[a]
  - Field spikes[a]

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a. If applicable.

- QC audit sample[a]
- Shipping dates
- Laboratories involved.

The chain-of-custody record includes sample descriptions and date of sampling. Although sampling date is not addressed by contract requirements, the reviewer must take into account lag time between sampling and shipping while assessing sample holding times.

a. If applicable.

4. PRECAUTIONS/LIMITATIONS

Within a given level of analytical support, there may be differences in the way individual laboratories or field operations approach internal QA/QC. For CLP routine analytical services (RAS) the procedures are standardized and contract-specific. When evaluating laboratory QA/QC, it is important for the reviewer to keep the requested level of analytical support in perspective. These levels produce data of different quality and documentation, and should be reviewed with this in mind. For example, it would be inappropriate to hold a screening laboratory to CLP RAS standards, or expect a field screening operation to have as rigorous QA/QC as a laboratory. Expectations such as these would be inconsistent with the concept of classifying analytical support by the quality of the data needed. Data quality objectives (DQOs)[5] are a vital starting point for time- and cost-effective project design.

DQOs should be clearly identified in the sampling and analysis plan (SAP).[6] The Environmental Restoration Program (ERP) SOW[7] that the laboratory is asked to use should be written such that the project's DQOs can be easily attained. If the requested and/or produced level of analytical support is insufficient to obtain the project's required DQOs, validation of the data will only document that the project's needs were not satisfied.

Data validation is only intended to evaluate the quality and reliability of data from laboratory analysis. Validation of the data does not take into account such things as project design and field sampling techniques.

Many EPA-approved inorganic analytical procedures are vague and open to individual interpretations. Analytical support levels other than level IV do not have any generally accepted data validation guidelines.

In order to be an effective data validator, one must be knowledgeable with analytical laboratory techniques and EPA QA/QC programs.

5. PREREQUISITES

The validator must have a copy of the laboratory data package, complete with reporting forms, chain-of-custody (COC) forms, and all raw data pages. The analytical SOW, copies of all pertinent method procedures, and validation guideline documentation must also be accessible to the data validator.

6. CALIBRATION/STANDARDIZATION

The CLP functional guidelines[2] will form the skeleton for the standardized inorganic data validation procedure. The CLP SOW is very descriptive with clearly outlined QA/QC requirements. Data validation for CLP-requested data is an extensive process, but the process is very routine and reproducible. Task-specific SOWs, general concepts from the CLP functional guidelines, and the data reviewer's analytical and validation experience are used for validating nonroutine and non-CLP data packages. Although nonroutine and non-CLP type data validation is usually more subjective and less reproducible than CLP type data validation, the data limitations and validation (L&V) report should explain the validator's reasoning for adding validation qualifier flags to the data and categorizing the data according to analytical levels.[7]

7. MATERIALS/EQUIPMENT

The data validator should have access to all required reference materials (e.g., inorganic CLP SOW, EPA SW-846, and standard methods), task-specific SOWs, computer with software capability for word processing and data unit conversions, calculator, office space, and office supplies.

8. INSTALLATION

Not applicable.

9. PROCEDURE

The CCS process can easily be performed concurrently with the technical validation if the data validator is intrinsically familiar with the ERP-mandated SOW used by the laboratory. Contractual and technical criteria are usually closely entwined; therefore, the data validator should report both contractual and technical anomalies observed during the validation process.

NOTE: Validation criteria is structured after the CLP functional guidelines.[2] Although these guidelines are based on requirements imposed by the CLP SOW on analytes from the CLP target analyte list (TAL), many of the guidelines also pertain to analytes not contained on the TAL. The validator must become familiar with the individual methods associated with any special analytical services (SAS) before SAS data can be properly validated.

Whenever applicable, the following requirements must be checked for compliance during the data validation process:

I. Holding Times

II. Calibration

- Initial

- Initial and Continuing Calibration Verification

III. Blanks

IV. ICP Interference Check Sample

V. Laboratory Control Sample

VI. Duplicate Sample

VII. Matrix Spike Sample

VIII. Furnace Atomic Absorption QC

IX. ICP Serial Dilution

X. Sample Result Verification

IX. Field Duplicates

XII. Overall Assessment of Data for a Case

I. HOLDING TIMES

A. Objective

The objective is to ascertain the validity of results based on the holding time of the sample from time of collection to time of analysis. For some analyses, the time from sample collection to sample preparation must also be considered.

NOTE: The holding time is based on the date of collection, rather than verified time of sample receipt, and date of digestion/distillation. It is a technical evaluation rather than a contractual requirement.

B. Criteria

Technical requirements for sample holding times have only been established for water matrices. The following holding time and preservation requirements were established under 40 CFR 136 (Clean Water Act) and are found in Volume 49, Number 209 of the Federal Register, page 43260, issued on October 26, 1984.

Metals: 6 months; preserved to pH < 2

Mercury: 28 days; preserved to pH < 2

Cyanide: 14 days; preserved to pH > 12

SAS: See requirements for EPA-approved methods.

C. Evaluation Procedure

Actual holding times are established by comparing the sampling date on the ERP COC forms with the dates of analysis found in the laboratory raw data (digestion logs and instrument run logs). Examine the digestion and/or distillation logs to determine if samples were preserved at the proper pH.

Analyte Holding Time (Days) = Analysis Date - Sampling Date.

NOTE: For some analyses, the time from sample collection to sample preparation must also be considered.

D. Action

1. If 40 CFR 136 criteria for holding times and preservation are not met, qualify all results greater than the (>) instrument detection limit (IDL) as estimated (J) and results less than the (<) IDL as estimated (UJ).

2. If holding times are exceeded by a factor of two or more, qualify the results as unusable (R).

3. The same validation qualifying criteria that is used for water sample holding times will also be used for soil samples.

II. CALIBRATION

A. Objective

Compliance requirements for satisfactory instrument calibration are established to ensure that the instrument is capable of producing acceptable quantitative data. Initial calibration demonstrates that the instrument is capable of acceptable performance at the beginning of the analysis run, and continuing calibration verification demonstrates that the initial calibration is still valid.

B. Criteria

1. Initial Calibration

Instruments must be calibrated daily and each time the instrument is set up.

a. ICP Analysis

A blank and at least one standard must be used in establishing the analytical curve.

b. Atomic Absorption Analysis (AA)

1) A blank and at least three standards, one of which must be at the contract required detection limit (CRDL), must be used in establishing the analytical curve.

2) The correlation coefficient must be $\geq$ 0.995.

NOTE: The correlation coefficient of 0.995 is a technical criterion and not contractual.

c. Mercury Analysis

1) A blank and at least four standards must be used in establishing the analytical curve.

2) The correlation coefficient must be $\geq$ 0.995.

d. Cyanide Analysis

1) A blank and at least three standards must be used in establishing the analytical curve.

2) A midrange standard must be distilled.

3) A correlation coefficient $\geq$ 0.995 is required for photometric determination.

e. SAS Analysis

1) A blank and at least four standards must be used in establishing the analytical curve unless stated otherwise in the task-specific SOW.

2) If applicable, a midrange standard must be distilled unless stated otherwise in the task-specific SOW.

2) The correlation coefficient must be $\geq$ 0.995 unless stated otherwise in the task-specific SOW.

2. Initial and Continuing Calibration Verification (ICV and CCV)

a. Analysis results must fall within the control limits of 90 to 110 percent Recovery (%R) of the true value for all analytes except mercury and cyanide.

b. Analysis results for mercury must fall within the control limits of 80 to 120 %R.

c. Analysis results for cyanide must fall within the control limits of 85 to 115 %R.

d. SAS analysis results must fall within the control limits of 90 to 110 %R of the true value unless stated otherwise in the task-specific SOW.

C. Evaluation Procedure

1. Verify that the instrument was calibrated daily and each time the instrument was set up using the correct number of standards and blanks.

2. Verify that the correlation coefficient is $\geq$ 0.995

3. Check the distillation log and verify that a midrange standard was distilled for cyanide (CN) and any applicable SAS analyte.

4. Review the results reported on the ICV and CCV summary report form [Form II - (part 1) for CLP analysis] as well as the raw data (ICP printouts, strip charts, printer tapes, bench sheets, etc.) for all ICVs and CCVs and verify that the results were accurately reported.

5. Recalculate all of the ICV and CCV %Rs using the following equation and verify that the recalculated value agrees with the laboratory reported values [Form II - (part 1) for CLP analysis]. Due to possible rounding discrepancies, allow results to fall within 1% of the contract windows (e.g., 89 to 111%).

$$\%R = \frac{\text{Found}}{\text{True}} \times 100$$

where

Found = concentration (in ug/L) of each analyte measured in the analysis of the ICV or CCV solution

True = concentration (in ug/L) of each analyte in the ICV or CCV source

D. Action

1. If the minimum number of standards as defined in Section B were not used for initial calibration, or if the instrument was not calibrated daily and each time the instrument was set up, qualify the data as unusable (R).

2. If the correlation coefficient is < 0.995, qualify results > IDL as estimated (J), and results < IDL as estimated (UJ).

   NOTE: For critical samples, further evaluation of the calibration curve may be warranted to determine if qualification is necessary.

3. If the midrange standard for CN or applicable SAS analytes were not distilled, qualify results > IDL as estimated (J), and results < IDL as estimated (UJ).

4. If the ICV or CCV %R falls outside the acceptance windows, qualify all associated data as follows:

   a. If the ICV or CCV %R falls outside the acceptance windows, but within the ranges of 75 to 89% or 111 to 125% (CN, 70 to 84% or 116 to 130%; Hg, 65 to 79% or 121 to 135%), qualify results > IDL as estimated (J).

   b. If the ICV or CCV %R is within the range of 111 to 125% (CN, 116 to 130%; Hg, 121 to 135%), results < IDL are acceptable.

c. If the ICV or CCV %R is 75 to 89% (CN, 70 to 84%; Hg, 65 to 79%), qualify results < IDL as estimated (UJ).

d. If the ICV or CCV %R is < 75%, (CN, < 70%; Hg, < 65%), qualify all results as unusable (R).

e. If the ICV or CCV %R is > 125%, (CN > 130%; Hg > 135%), qualify results > IDL as unusable (R); results < IDL are acceptable.

III. BLANKS

A. Objective

The assessment of blank analysis results is to determine the existence and magnitude of contamination problems. The criteria for evaluation of blanks applies to any blank associated with the samples. If problems with any blank exist, all data associated with the case must be carefully evaluated to determine whether or not there is an inherent variability in the data for the case, or if the problem is an isolated occurrence not affecting other data.

B. Criteria

No contaminants should be in the blank(s).

C. Evaluation Procedures

Review the results reported on the blank summary report form (Form III for CLP analysis) and the raw data (ICP printouts, strip charts, printer tapes, bench sheets, etc.) for all blanks and verify that the results were accurately reported.

D. Action

1. Sample results > IDL but < five times (5x) the highest positive amount in any blank should be qualified as (U).

2. If any blank associated with the samples has a negative result whose absolute value is > two times (2x) the IDL proceed as follows:

   a. If the sample value is < the IDL qualify the results as estimated (UJ).

   b. If the sample value is > the IDL but < five times (5x) the highest absolute value of any negative blank qualify the results as estimated (J).

   c. Sample values ≥ 5x the highest absolute value of any negative blank are acceptable.

3. If any sample result is negative and has an absolute value > two times (2x) the IDL qualify the results as estimated (UJ).

NOTE: The blank analyses may not involve the same weights, volumes, or dilution factors as the associated samples. In particular, soil sample results reported on CLP Form I will not be on the same basis (units, dilution) as the calibration blank data reported on CLP Form III. The reviewer may find it easier to work from the raw data when applying 5X criteria to soil sample data/calibration blank data.

In instances where more than one blank is associated with a given sample, qualification should be based upon a comparison with the associated blank having the highest concentration of a contaminant. The results must not be corrected by subtracting any blank value unless specifically outlined in the SAS method.

IV. ICP INTERFERENCE CHECK SAMPLE (ICS)

A. Objective

The ICP interference check sample (ICS) verifies the laboratory's interelement and background correction factors.

B. Criteria

1. An ICS must be run at the beginning and end of each sample analysis run (or a minimum of twice per 8-hour working shift, whichever is more frequent).

2. Results for the ICS solution AB analysis must fall within the control limits of ± 20% of the true value.

C. Evaluation Procedure

1. Recalculate from the raw data (ICP printout) all of the recoveries using the following equation (%R) and verify that the recalculated values agree with the laboratory reported values (Form IV for CLP analysis).

$$\text{ICS \%R} = \frac{\text{Found Solution AB}}{\text{True Solution AB}} \times 100$$

where

Found Solution AB = concentration (in ug/L) of each analyte measured in the analysis of solution AB

True Solution AB = concentration (in ug/L) of each analyte in solution AB

2. Check ICS raw data for results with an absolute value > IDL for those analytes that are not present in the ICS solution.

D. Action

1. For samples with concentrations of Al, Ca, Fe, and Mg that are comparable to or greater than their respective levels in the ICS:

   a. If the ICS recovery for an element is > 120% and the sample results are < IDL, these data are acceptable for use.

   b. If the ICS recovery for an element is > 120% and the sample results are > IDL, qualify the affected data as estimated (J).

   c. If the ICS recovery for an element falls between 50 and 79% and the sample results are > IDL, qualify the affected data as estimated (J).

   d. If sample results are < IDL and the ICS recovery for that analyte falls within the range of 50 to 79%, the possibility of false negatives may exist. Qualify the data for these samples as estimated (UJ).

   e. If ICS recovery results for an element fall < 50%, qualify the affected data as unusable (R).

2. If results > IDL are observed for elements that are not present in the EPA-provided ICS solution, the possibility of false positives exists. An evaluation of the associated sample data for the affected elements should be made. For samples with comparable or higher levels of interferents and with analyte concentrations that approximate those levels found in the ICS (false positives), qualify sample results > IDL as estimated (J).

3. If negative results are observed for elements that are not present in the EPA ICS solutions, and their absolute value is > IDL, the possibility of false negatives in the samples may exist. If the absolute value of the negative results is > IDL, an evaluation of the associated sample data should be made. For samples with comparable or higher levels of interferents, qualify results for the affected analytes < IDL as estimated (UJ).

4. In general, the sample data can be accepted if the concentrations of Al, Ca, Fe, and Mg in the sample are found to be less than or equal to their respective concentrations in the ICS. If these elements are present at concentrations greater than the level in the ICS, or other elements are present in the sample at > 100 mg/L, the reviewer should investigate the possibility of other interference effects by using Table 2 given on page D-30 of the March 1990 SOW. These analyte concentration equivalents presented in the table should be considered only as estimated values, since the exact value of any analytical system is instrument-specific. Therefore, estimate the concentration produced by an interfering element. If the estimate is > 2X CRDL and also greater than 10% of the reported concentration of the affected element, qualify the affected results as estimated (J).

V. LABORATORY CONTROL SAMPLE (LCS)

A. Objective

The laboratory control sample (LCS) serves as a monitor of the overall performance of all steps in the analysis, including the sample preparation.

Criteria

1. All aqueous LCS results must fall within the control limits of 80 to 120 %R, except Sb and Ag, which have no control limits.

2. All solid LCS results must fall within the control limits established by the EPA. This information is available from EMSL/LV. (NOTE: If an EPA LCS is unavailable to the laboratory, a commercial product may be substituted provided that the control limits are documented.)

C. Evaluation Procedure

1. Review the LCS report summary form (Form VII for CLP analysis) and verify that results fall within the control limits.

2. Check the raw data (ICP printout, strip charts, bench sheets, etc.) to verify the reported recoveries on the LCS report summary form (Form VII for CLP analysis). Recalculate all of the recoveries (%R) using the following equation:

$$\text{LCS \%R} = \frac{\text{LCS FOUND}}{\text{LCS True}} \times 100$$

where

LCS Found = concentration (in ug/L for aqueous; mg/kg for solid) of each analyte measured in the analysis of LCS solution

LCS True = concentration (in ug/L for aqueous; mg/kg for solid) of each analyte in the LCS source.

D. Action

1. Aqueous LCS

a. If the LCS recovery for any analyte falls within the range of 50 to 79% or > 120% but < 150%, qualify results > IDL as estimated (J).

b. If results are < IDL and the LCS recovery is > 120%, the data are acceptable.

c. If results are < IDL and the LCS recovery falls within the range of 50 to 79%, qualify the data for the affected analyte as estimated (UJ).

d. If LCS recovery results are < 50% or > 150%, qualify the data for these samples as unusable (R).

2. Solid LCS

a. If the solid LCS recovery for any analyte falls outside the documented control limits, qualify all sample results > IDL as estimated (J).

b. If the LCS results are higher than the control limits and the sample results are < IDL, the data are acceptable.

c. If the LCS results are lower than the control limits, qualify all sample results < IDL as estimated (UJ).

VI. DUPLICATE SAMPLE ANALYSIS

A. Objective

Duplicate analyses are indicators of laboratory precision based on each sample matrix.

B. Criteria

1. Samples identified as field blanks cannot be used for duplicate sample analysis.

2. A control limit of ± 20% (35% for soil) for the relative percent difference (RPD) shall be used for sample values > 5X CRDL.

3. A control limit of ± CRDL (± 2X CRDL for soil) shall be used for sample values < 5X CRDL, including the case when only one of the duplicate sample values is < 5X CRDL.

C. Evaluation Procedure

1. Review the duplicate summary form (Form VI for CLP analysis) and verify that results fall within the control limits.

2. Check the raw data and recalculate all RPDs using the following equation to verify that results have been correctly reported on the duplicate summary form (Form VI for CLP analysis).

$$RPD = \frac{[S-D]}{(S+D)/2} \times 100$$

where

S = first sample value (original)
D = second sample value (duplicate).

3. If possible, verify that the field blank was not used for duplicate analysis.

D. Action

1. If duplicate analysis results for a particular analyte fall outside the appropriate control windows, qualify the results for that analyte in all associated samples of the same matrix as estimated (J).

2. If the field blank was used for duplicate analysis, all other QC data must be carefully checked and professional judgement exercised when evaluating the data.

NOTE: This information must be included on the inorganic regional data assessment (IRDA) form.

VII. MATRIX SPIKE SAMPLE ANALYSIS

A. Objective

The matrix spike sample analysis provides information about the effect of each sample matrix on the digestion and measurement methodology.

B. Criteria

1. Samples identified as field blanks cannot be used for spiked sample analysis.

2. Spike recovery (%R) must be within the limits of 75 to 125%. However, spike recovery limits do not apply when sample concentration exceeds the spike concentration by a factor of four or more.

C. Evaluation Procedure

1. Review the spike summary forms (Form V for CLP analysis) and verify that results fall within the specified limits.

2. Check raw data and recalculate all of the %Rs using the following equation to verify that results were correctly reported on the spike summary forms (Form V for CLP analysis).

$$\%R = \frac{(SSR-SR)}{SA} \times 100$$

where

SSR = spiked sample result
SR = sample result
SA = spike added.

3. If possible, verify that the field blank was not used for spike analysis.

D. Action

1. If the spike recovery is > 125% and the reported sample results are < IDL, the data are acceptable for use.

2. If the spike recovery is > 125% and ≤ 170% or < 75% and the sample results are > IDL, qualify the data for these samples as estimated (J).

3. If the spike recovery falls within the range of 30 to 74% and the sample results are < IDL, qualify the data for these samples as estimated (UJ).

4. If spike recovery results are < 30% and the sample results are < IDL, qualify the data for these samples as unusable (R).

5. If spike recovery results are > 170% and the sample results are > IDL, qualify the data for these samples as unusable (R).

6. If the field blank was used for matrix spike analysis, all other QC data must be carefully checked and professional judgement exercised when evaluating the data.

NOTE: This information must be included on the IRDA form.

NOTE: If the matrix spike recovery does not meet criteria (except [illegible] Hg), a post-digestion spike is required for all methods except furnace, but these data are not used to qualify sample results. However, this information must be included in the IRDA report.

VIII. FURNACE ATOMIC ABSORPTION QC

A. Objective

Duplicate injections and furnace analytical spikes establish the precision and accuracy of the individual instrument determinations.

B. Criteria

1. For sample concentrations > CRDL, duplicate injections must agree within ± 20% RSD, [or coefficient of variation (CV)], otherwise the sample must be rerun once (at least two additional injections).

2. Analytical spike recovery must be ≥ 85% and ≤ 115%.

3. The furnace atomic absorption scheme must be followed as described in the March 1990 SOW, p. E-24.

C. Evaluation Procedure

1. Check raw data to verify that duplicate injections agree within ± 20% RSD (or CV) for sample concentrations > CRDL.

2. Review furnace AA raw data to verify that the furnace atomic absorption scheme has been followed.

D. Action

1. If duplicate injections are outside the ± 20% RSD (or CV) limits and the sample has not been rerun once as required, qualify the data as estimated (J).

2. If the rerun sample results do not agree within ± 20% RSD (or CV), qualify the data as estimated (J).

3. If the analytical spike recovery is < 40%, for analyses within the calibration range, for both the original and repeated analysis, qualify results as unusable (R).

4. If the analytical spike recovery is ≥ 40% and the sample absorbance is < 50% of the analytical spike absorbance, proceed as follows:

   a. If the results are < IDL and the analytical spike recovery is ≥ 115%, the data are acceptable.

   b. If the analytical spike recovery is ≥ 40% but < 80%, qualify results < IDL as estimated (UJ).

   c. If the analytical spike recovery is ≥ 40% and < 80%, or > 120% and ≤ 160%, qualify results > IDL as estimated (J).

   d. If the analytical spike recovery is > 160%, qualify results > IDL as unusable (R).

5. If the method of standard additions (MSA) is required but has not been done, qualify the data as estimated (J).

6. If any of the samples run by MSA have not been spiked at the appropriate levels, qualify the data as estimated (J).

7. If the MSA correlation coefficient is < 0.995, qualify the data as estimated (J).

IX. ICP SERIAL DILUTION

A. Objective

The serial dilution determines whether significant physical or chemical interferences exist due to sample matrix.

B. Criteria

If the analyte concentration is sufficiently high (concentration in the original sample is minimally a factor of 50 above the IDL), an analysis of a five-fold dilution must agree within 10% Difference (%D) of the original results.

C. Evaluation Procedures

1. Check the raw data and recalculate the %Ds using the following equation to verify that the dilution analysis results agree with results reported on the serial dilution summary forms (Form IX for CLP analysis).

$$\%D = \frac{[I-S]}{I} \times 100$$

where

I = initial sample result
S = serial dilution result (instrument reading x 5).

Check the raw data for evidence of negative interference, e.g., results of the diluted sample are significantly higher than the original sample.

D. Action

1. If the analyte concentration is sufficiently high (concentration in the original sample is minimally a factor of 50 above the IDL) and the %D is > 10% but ≤ 40%, qualify the associated data as estimated (J).

2. If the analyte concentration is sufficiently high (concentration in the original sample is minimally a factor of 50 above the IDL) and the %D is > 40%, qualify the associated data as unusable (R).

3. If evidence of negative interference is found, use professional judgement to qualify the data.

X. SAMPLE RESULT VERIFICATION

A. Objective

The objective is to ensure that the reported quantitation results are accurate.

B. Criteria

Analyte quantitation must be calculated according to the appropriate SOW.

C. Evaluation Procedures

The raw data should be examined to verify the correct calculation of sample results reported by the laboratory. Digestion and distillation logs, instrument printouts, strip charts, etc., should be compared to the reported sample results.

1. Examine the raw data for any anomalies (baseline shifts, negative absorbances, omissions, legibility, etc.).

2. Verify that there are no transcription or reduction errors (e.g., dilutions, percent solids, sample weights) on any of the samples.

3. Verify that results fall within the linear range of the ICP (Form XIII for CLP analysis) and within the calibrated range for any non-ICP parameters.

4. Verify that sample results are > 5X ICP IDL, if ICP analysis results are used for As, Tl, Se, Pb, or any other analyte that does not meet the required detection limit.

NOTE: When the laboratory provides both ICP and furnace results for an analyte in a sample and the concentration is > ICP IDL, the results can assist in identifying quantitation problems.

D. Action

If there are any discrepancies found, the laboratory may be contacted by the designated representative to obtain additional information that could resolve any differences. If a discrepancy remains unresolved, the reviewer may determine that qualification of the data is warranted.

XI. FIELD DUPLICATES

A. Objective

Field duplicate samples may be taken and analyzed as an indication of overall precision. These analyses measure both field and laboratory precision; therefore, the results may have more variability than laboratory duplicates, which measure only laboratory performance. It is also expected that soil duplicate results will have a greater variance than water matrices because of difficulties associated with collecting identical field samples.

B. Criteria

There are no review criteria for field duplicate analyses comparability.

C. Evaluation Procedures

If field duplicates have been identified for the validator, the RPD should be calculated.

D. Action

Any evaluation of the field duplicates should be provided with the reviewer's comments.

XII. OVERALL ASSESSMENT OF DATA FOR A CASE

It is appropriate for the data reviewer to make professional judgements and express concerns and comments on the validity of the overall data for a case. This is particularly appropriate when there are several QC criteria out of specification. The additive nature of QC factors out of specification is difficult to assess in an objective manner, but the reviewer has a responsibility to inform the user concerning data quality and data limitations in order to assist that user in avoiding inappropriate use of the data, while not precluding any consideration of the data at all. If qualifiers other than those used in this document are necessary to describe or qualify the data, it is necessary to thoroughly document/explain the additional qualifiers used. The data reviewer would be greatly assisted in this endeavor if the DQOs were provided. The IRDA form and supplementary documentation must be included with the review.

10. CALCULATIONS

All calculations must be checked for accuracy if the validation is to be considered complete. The RAS calculation procedures that are used to determine such things as MSA values, duplicate RPDs, serial dilution percent differences, and percent recoveries for ICVs, CCVs, CRDL standards, ICSs, spikes, and LCSs, will be outlined in the inorganic CLP SOW. Calculation procedures for producing data for SAS analyses will be outlined in standard analytical methods and/or task-specific SOWs. Calculation errors should only be rectified by resubmission of corrected data sheets by the laboratory that originally generated the data.

11. DATA REDUCTIONS

All data reductions must be checked for accuracy if the validation is to be considered complete. Digestion weights, percent solids, digestate volumes, and sample dilutions must all be accounted for when reducing data directly from instrumentation printouts. Unit conversions must be checked for accuracy during the validation process. Anomalies between the raw data and the reported results must be noted by the validator. Mistakes, such as unit conversion and transcription errors, should only be rectified by resubmission of corrected data sheets by the laboratory that originally generated the data.

12. DATA REPORTING

An L&V report must be written for every data package that is validated. [NOTE: A data package will consist of only one sample delivery group (SDG) unless specifically requested otherwise by the customer that solicits data validation.] The L&V report will conform to the following format:

A. TITLE

The title of the report will be: INORGANIC DATA LIMITATIONS and VALIDATION REPORT. Also included in the title name will be the name of the project site, sample type, analysis type, and SDG identification number.

B. INTRODUCTION

The introduction section of the report should describe the analytical and validation schemes that were used for the project.

C. CONTRACT AND TECHNICAL REVIEW

The first part of the Contract and Technical Review (CTR) section must list the site location, type of analyses, SDG number, laboratory name, and field and laboratory identification numbers for all samples contained in the SDG. The second part of the CTR section must contain numerically listed comments that describe all observations and findings that the validator concludes are in need of being brought to the attention of the project manager, end data users, and/or the data producing laboratory personnel. The reasons behind any sample receiving validation qualifying flags must be contained in the CTR comments section. (See Appendix A for example).

D. DATA LIMITATION OVERVIEW

This section of the report will describe the quality of data based on sample matrix interferences and the laboratory's adherence to good laboratory practice and QC measures. The Data Limitation Overview will be subdivided into the following four sections:

a. Summary of Qualified Data

This section must list all samples and their respective analytes that were given validation qualifying flags. A reference must also be made to all CTR comment numbers that pertain to a value being flagged.

b. Inorganic Regional Data Assessment

The IRDA form contained in Reference 2, or one of similar content, must be filled in to describe the data assessment as accurately as possible. If mandatory actions are required, they should be specifically noted on this form. In addition, this form is to be used to summarize overall deficiencies requiring attention, as well as general laboratory performance and any discernible trends in the quality of the data. This form is not a replacement for the data review. Sufficient supplementary documentation must accompany the form to clearly identify the problems associated with the data. (See Appendix B for example.)

c. Data Validation Flag Table

A table, listing all the field identification numbers and all of the analytes tested for, must be filled in with all the qualifying flags introduced by the data validator. (See Appendix C for example.)

d. Summary of Data Usability

The percentage of completeness of the data and the associated level of usability as described in Reference 5 must be listed in this summary.

E. LABORATORY APPRAISAL

This section is reserved for laboratory performance evaluation. Any noteworthy attributes or deficiencies should be listed here.

F. REFERENCES

All reference material that was used to validate the data should be listed here.

13. METHOD PERFORMANCE

Individual validators that are intrinsically familiar with CLP protocol and who have an understanding of good laboratory practices should be able to produce comparable L&V report for RAS analyses. Although SAS analyses will usually produce more subjective L&V reports, knowledgeable validators should be able to prevent bad data from being unqualified during the validation process.

14. REFERENCES

1. EG&G Idaho, Inc., Environmental Restoration Program, Program Directive 5.11, "Preparation and Use of DOPs and SOPs."

2. *Laboratory Data Validation Functional Guidelines For Evaluating Inorganic Analyses*, compiled by Ruth Bleyler, Sample Management Office, Viar & Company, prepared by the USEPA Data Review Work Group, July 1, 1988.

3. Margaret A. Hellmann and Richard A. Cheatham, *Data Validation, Its Importance in Health Risk Assessments*; ES&T, vol 23. No. 6, 1989.

4. EG&G Idaho, Inc., Environmental Restoration Program, Program Directive 5.8, "Control of Nonconforming Analytical Data."

5. *Data Quality Objectives for Remedial Response Activities*, EPA/540/G-87/003, March 1987.

6. EG&G Idaho, Inc., Environmental Restoration Program, Program Directive 5.2, "Preparation of Sampling and Analysis Plans."

7. EG&G Idaho, Inc., Environmental Restoration Program, Program Directive 5.5, "Obtaining Laboratory Services."

APPENDIX A

CONTRACT AND TECHNICAL REVIEW

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APPENDIX A

CONTRACT and TECHNICAL REVIEW

Site: BJS Industrial Waste Pond
Type: Metals
SDG No.: EG001010HU
Laboratory: AceLabs

Sample Identification:

FIELD ID	LAB ID
EG001010HU	91000465
EG002010HF	91000467
EG003010HU	91000494
EG004010HF	91000495
EG005010HF	91000519
EG006010HU	91000520
EG007010HF	91000605
EG008010HU	91000606
EG009010HFS	91000615
EG010010HUS	91000616
EG011010HF	91000621
EG012010HU	91000622
EG013010HF	91000623
EG014010HU	91000624
EG015010HF1	91000631
EG016010HU1	91000632
EG017010HF	91000636
EG018010HU	91000638
EG01910HFS	91000674
EG020010HFS	91000675

COMMENTS:

1) Some of the data on the instrument printouts were crossed out without being dated and initialed (e.g., see raw data pages 138 and 312).

2) The selenium matrix spike recovery of 59.7% was substantially below the lower control limit of 75%. All selenium results will therefore be flagged at a minimum with either a "J" or "UJ" validation qualifying flag.

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APPENDIX B

INORGANIC REGIONAL DATA ASSESSMENT

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APPENDIX B

Region _____

INORGANIC REGIONAL DATA ASSESSMENT

CASE NO. _____ SITE _____

LABORATORY _____ NO. OF SAMPLES/ MATRIX _____

SDG# _____ REVIEWER (IF NOT ESD) _____

SOW# _____ REVIEWER'S NAME _____

DPO: ACTION _____ FYI _____ COMPLETION DATE _____

DATA ASSESSMENT SUMMARY

		ICP	AA	Hg	CYANIDE
1.	HOLDING TIMES				
2.	CALIBRATIONS				
3.	BLANKS				
4.	ICS				
5.	LCS				
6.	DUPLICATE ANALYSIS				
7.	MATRIX SPIKE				
8.	MSA				
9.	SERIAL DILUTION				
10.	SAMPLE VERIFICATION				
11.	OTHER QC				
12.	OVERALL ASSESSMENT				

O = Data had no problems/or qualified due to minor problems.
M = Data qualified due to major problems.
Z = Data unacceptable.
X = Problems, but do not affect data.

ACTION ITEMS: _____

_____

AREAS OF CONCERN: _____

_____

NOTABLE PERFORMANCE: _____

_____

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APPENDIX C

DATA VALIDATION FLAG TABLE

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APPENDIX C

DATA VALIDATION FLAG TABLE
(SDG# EG001010HU)

	PARAMETERS																					
FIELD ID	Al	Sb	As	Ba	Be	Cd	Ca	Cr	Co	Cu	Fe	Pb	Mg	Mn	Hg	Ni	K	Se	Ag	Na	Tl	V	Zn
EG001010HU		J	J															J	J	R			
EG002010HF		UJ	J									UJ						UJ	J				
EG003010HU		J	J															R			J		
EG004010HF		UJ	J									UJ						J	J				
EG005010HF		UJ																UJ					
EG006010HU		UJ																UJ					
EG007010HF		UJ																UJ					
EG008010HU		UJ																UJ					
EG009010HFS		UJ																UJ					
EG010010HUS		UJ																UJ					
EG011010HF		J																UJ					
EG012010HU																		UJ					
EG013010HF		UJ																UJ					
EG014010HU		UJ																UJ	UJ				
EG015010HF1																		UJ					
EG016010HU1							R											UJ	UJ				
EG017010HF																		J					
EG018010HU																		J					
EG019010HFS		J								R								J					
EG020010HFS																		J			R		

APPENDIX C (continued)

U - The material was analyzed for, but was not detected above the level of the associated value. The associated value is either the sample quantitation limit or the sample detection limit.

J - The analyte was analyzed for and was positively identified, but the associated numerical value may not be consistent with the amount actually present in the environmental sample.

R - The data are unusable.

UJ - The material was analyzed for, but was not detected. The associated value is an estimate and may not accurately reflect the IDL in the sample matrix.